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DRAWINGS ATTACHED

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(54) PHOTOGRAPHIC MULTI-COLOUR SILVER HALIDE MATERIAL

(71) We, VEB FILMFABRIK WOLFEN, a Company recognised under German Law, of Wolfen, Kreis Bitterfeld, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides photographic multi-colour silver halide material which is specially suitable for making colour prints. Materials for colour printing must satisfy special requirements with respect to sharpness and resolution in order to obtain complete reproduction of all that is contained in the negative.

It is known that properties of sharpness can be improved not only by variations in casting, for example by using thin-layer casting and layer exchange, but also by adding suitable substances to the emulsions, for example filter dyes. As is known the undesired halation caused by blue light in the silver halide emulsion layers may be reduced by dyeing the layer with a yellow dye. The halation produced by green or red scattered light in the emulsion layers may also be reduced by dyeing them with red or green or cyan screening dyes.

To obtain optimal results in the printing process, the green or cyan screening dyes suitable for use in red-sensitive layers for example must satisfy a variety of conditions: First of all, the dyes must display the desired absorption in the red spectral region, especially between 630 and 700 nm, without disturbing secondary absorption in the green and blue spectral regions. Furthermore, it is necessary to bleach completely or remove the dyes in the photographic baths; they must have as high a molecular density as possible and must not produce any disturbing side effects in contact with the other photochemical additives to the emulsions, for example sensitizers, stabilizers, colour couplers and wetting agents.

Screening dyes that possess all of these favourable properties are very rare in practice.

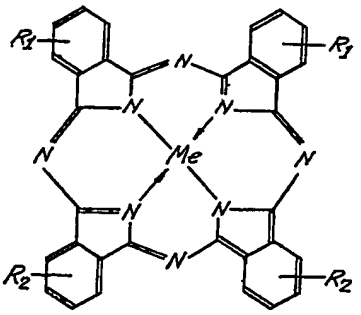
Thus, for example, anthraquinone dyes have insufficient absorption and consequently satisfy these demands only to a limited extent. Iron complex salts of the 1,2-naphthylene-diamine disulphonic acids, as proposed in German Published Specification 1,152,609, are insufficiently selective in the green and especially the blue spectral region, which causes an undesired loss of sensitivity in an underlying blue-sensitized emulsion layer. In German Specification 694,186 phthalocyanine dyes are mentioned which are completely unsuitable in practice because they are substantive. Belgian Specification 710,095 describes phthalocyanine dyes which do give quite useful results but their absorption bands are very narrow; this means that a part of the red light can still pass through the emulsion layer and may produce undesired scattering effects.

It is therefore an object of the present invention to improve multi-layer colour photographic material for printing purposes insofar as its reproductivity is concerned.

The task is therefore to provide cyan and green screening dyes suitable for use in the red-sensitive layer of photographic multi-colour silver halide materials which do not impair the photographic and sensitometric properties of the material and ensure complete protection against red scattered light together with an improvement in outline sharpness and resolution of materials manufactured with their use.

The present invention is based on the observation that the objective can be accomplished by adding to the red-sensitive silver halide emulsion layer of a multi-colour photographic material which uses development by a colour developer in the presence of colour couplers, a

cyan and/or green water-soluble phthalocyanine screening dye of the general formula



in which

Me=Cu, Ni, Cr, Al, Fe

$R_1=SO_2NHR_3$

$R_2=$ $SO_2—NH—R_4$, $SO_2—NH—NH—COO—C_2H_5$, $SO_2—NH—NH—(CH_2)_3—SO_3H$, $SO_2—NH—NH_2$, $SO_2—NH—SO_2—NH_2$ or $SO_2—NH—NH—CS—NH_2$

$R_3=H$, $NH—R_4$, an alkyl- or aryl residue which may be substituted, $CONH_2$, $CSNH_2$, $C(NH)NH_2$ or SO_2NH_2

$R_4=H$, an alkyl- or aryl residue which may be substituted, $CONH_2$, $COOC_2H_5$, $CSNH_2$ or $C(NH)NH_2$.

The dyes of this invention may be incorporated in the form of an aqueous solution with the red-sensitive emulsion layer before casting in an amount of 0.25 g to 3 g, preferably 0.75 g per kg of emulsion. The dyes of the invention may be manufactured by the methods described in the literature, for example by F. H. Moser and A. L. Thomas in Phthalocyanine Compounds, London, 1963, or Fierz-David and Blangey in "Farbenchemie", 8th Edition 1952. A special advantage of the dyes of the invention is the broadening of the absorption curves in the red spectral region, as can be seen by the appearance of two maxima which have very steep flanks towards both the shortwave and the longwave side of the spectrum. This ensures excellent permeability in both the green and the blue spectral region.

The following Table indicates a number of dyes according to the invention, together with their relevant absorption maxima, which are particularly suitable for use according to the invention.

In each column the substituents Me, R_1 and R_2 refer to the above general formula and the relevant absorption maximum in nm is given.

TABLE

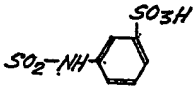
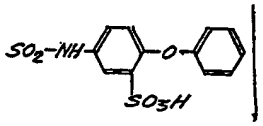
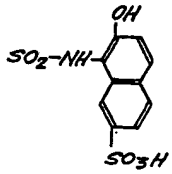
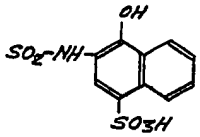
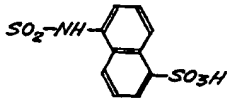
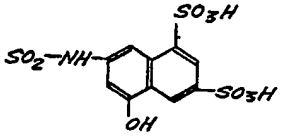
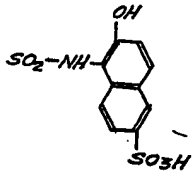
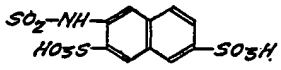
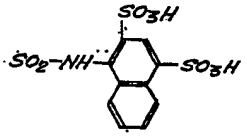
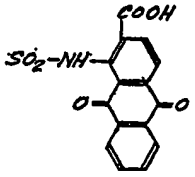
Dyestuff	Me	R_1	R_2	Absorption maximum in nm
I	Cu	$SO_2—NH_2$	same as R_1	628/668
II	Cu		"	635/670
III	Ni	$SO_2—NH—CH_2—COOH$	"	630/665
IV	Cu	$SO_2—NH—CH_2—COOH$	"	635/668
V	Cu		"	638/665
VI	Cu	$SO_2—NH—NH—COOC_2H_5$	"	640/670
VII	Cu	$SO_2—NH—NH—(CH_2)_3—SO_3H$	"	634/668
VIII	Cu	$SO_2—NH—SO_2—NH_2$	"	635/670
IX	Cu	$SO_2—NH—NH—CS—NH_2$	"	635/672
X	Cu	$SO_2—NH—NH_2$	"	640/670
XI	Cu	$SO_2—NH—CS—NH_2$	"	630/670

TABLE (Continued)

Dyestuff	Me	R_1	R_2	Absorption maximum in nm
XII	Cu	SO_2—NH—CO—NH_2	same as R_1	640/674
XIII	Cu	SO_2—NH—C(NH)—NH_2	"	640/672
XIV	Cu		"	636/668
XV	Cu		"	637/668
XVI	Cu		"	636/670
XVII	Cu		"	640/672
XVIII	Cu		"	640/670
XIX	Cu		"	634/665
XX	Cu		"	638/672
XXI	Cu		"	640/674

The accompanying graph shows the typical absorption curves of aqueous solutions of 0.001% strength of the dyes I, IX and XVIII according to the invention. For comparison an absorption curve of a dye according to Belgian Specification 710,095 (curve O) is also shown. The Figure shows the characteristic development of the curves of the dyes according to the invention having two equivalent absorption maxima in the red spectral region as well as very good permeabilities in the green and blue spectral regions.

The high extinctions of the dyes of this invention are especially valuable. The molecular weights of the dyes have not been considered in this comparison.

The following Examples illustrate the invention.

EXAMPLE 1.

A red-sensitive silver chlorobromide emulsion is produced on a photographic layer support which may consist of acetylcellulose or another suitable polymeric material. One kilogram of emulsion contains 30 mg of Red Sensitizer Rr 1953 (Bios Final Report 721,10; 1946), 15 g of cyan forming coupler F 546 (Bios Final Report 721,23; 1946), 0.75 g of the dye I according to this invention as well as a stabilizer and a wetting agent (material A).

In identical manner a material is prepared which contains no screening dye (material B). The materials are exposed under a line screen, colour-developed in a solution containing N,N-diethyl-para-phenylenediamine, bleached, fixed, washed and dried and then subjected to microscopic evaluation. Material A gave a resolution of 130 lines per mm and material B 100 lines per mm.

EXAMPLE 2.

When the procedure described in Example 1 is used and a colour photographic layer is manufactured which contains the dye II instead of the dye I according to this invention, a resolution of 130 lines per mm is obtained.

EXAMPLE 3.

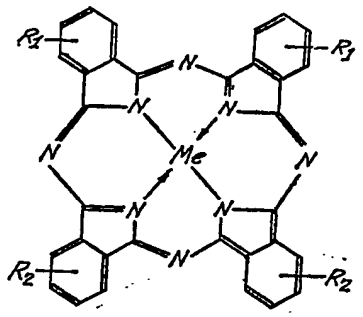
The following layers are produced in the known manner on a photographic support: (a) a blue-sensitive silver bromide emulsion which contains per kg 18 g of yellow-forming coupler F 535 (Bios Final Report 721,22; 1946) as well as a suitable stabilizer, a wetting agent, a hardener and also if desired a polymeric plasticizer; (b) an interlayer; (c) a red-sensitized silver chlorobromide emulsion containing per kg 15 g of cyan-forming coupler F 546 (Bios Final Report 721,23; 1946), 30 mg of red sensitizer Rr 1953 (Bios Final Report 721,10; 1946), 0.75 g of screening dye XVIII according to this invention, as well as a suitable stabilizer, a wetting agent, a hardener and also if desired, a polymeric plasticizer; (d) an interlayer; (e) a green-sensitized silver chlorobromide emulsion containing per kg 18 g of magenta-forming coupler 1-(4'-phenoxy-3'-sulphophenyl) - 3 - stearoylamino - pyrazolone-(5), 20 mg of green sensitizer Rr 340 (Bios Final Report 721,7; 1946) as well as the usual additives (material C).

In identical manner a multi-layer material is prepared which contains no dye according to this invention in the red-sensitized emulsion layer (material D).

When the printing materials prepared as described in Example 3 are exposed under the same colour negative, the print on material C displays a distinctly improved sharpness. This visual impression is confirmed by determining the outline sharpness (H. Frieser, Agfa Mitteilungen I, 1955, page 29; Photo-Korrespondenz 91,69; 1955, 92,51; 1956). For material C a value of 30μ and for material D a value of 50μ were found in the red-sensitized layer.

WHAT WE CLAIM IS:—

1. A photographic multi-colour silver halide material which uses development by a colour developer in the presence of colour couplers and in which the red-sensitive silver halide emulsion layer contains a filter dye of the general formula



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R_3 = H, NH—R_4, an alkyl- or aryl residue which may be substituted, $CONH_2$, $CSNH_2$, $C(NH)NH_2$ or SO_2NH_2

R_4 = H, an alkyl- or aryl residue which may be substituted, $CONH_2$, $COOC_2H_5$, $CSNH_2$ or $C(NH)NH_2$.

2. A photographic multi-colour material as claimed in claim 1, in which the red-sensitive emulsion layer before casting, contains 0.25 g to 3 g of dyestuff per kilogram of emulsion.

3. A photographic multi-colour material as claimed in claim 2, wherein the quantity of the filter dyestuff is 0.75 g per kilogram of emulsion.

4. A photographic multi-colour material as claimed in claim 1, obtained substantially as

described in the Examples or with reference to the Table herein.

5. A process for the production of photographic multi-colour material as claimed in claim 1, conducted substantially as described and exemplified herein.

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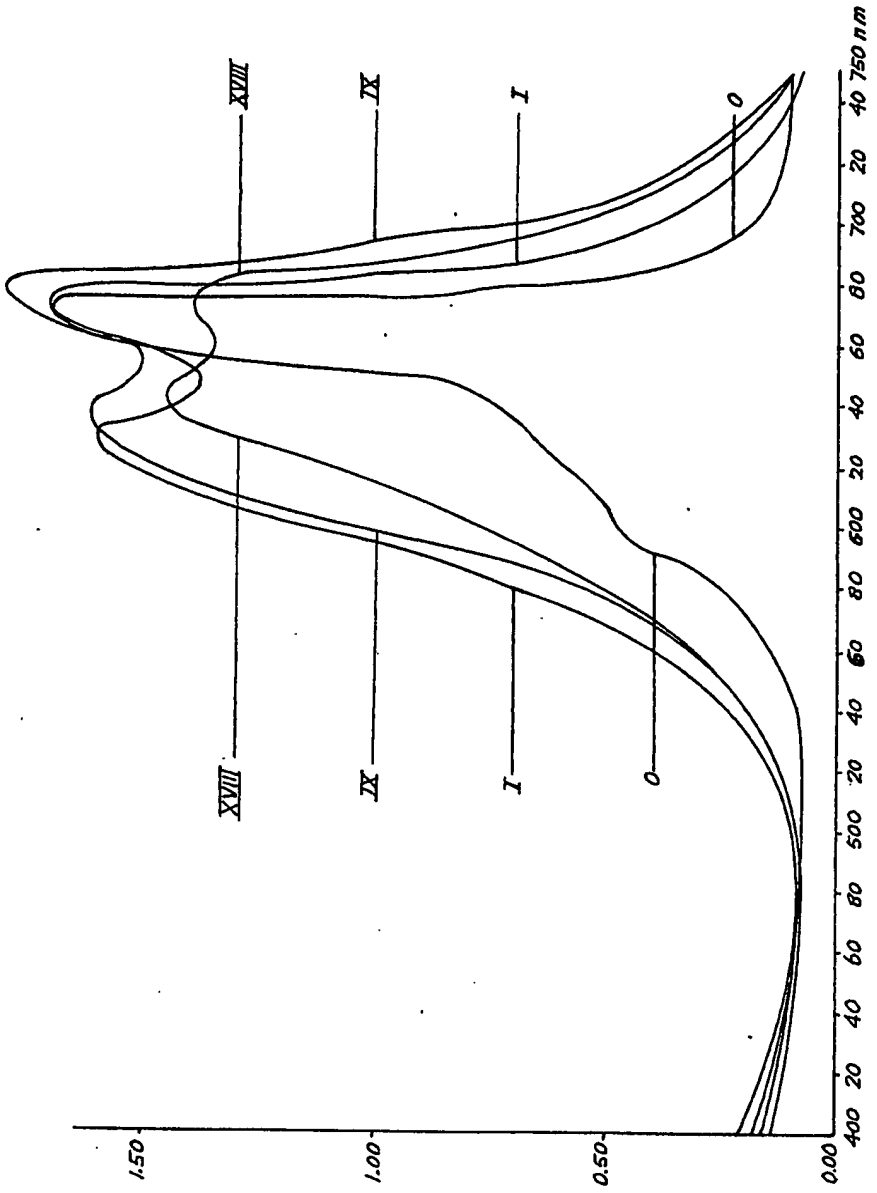

DENSITY IN LOGARITHMIC UNITS.